

Simulation of eucalyptus bio-oil and Brazilian crude oils blends distillation: effects, challenges and opportunities.

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Abstract. Potentially obtained from different sources, in particular from agro-industrial feedstocks such as sugarcane, soybean and eucalyptus - all abundant in Brazil - the complex, acidic and unstable fast pyrolysis bio-oil mixture of components presents opportunities and challenges to compose production routes of renewable fuels and chemicals. So far, most of coprocessing efforts were towards its blending with VGO in FCC, which presented good products quality and satisfactory renewable carbon captured in liquid output. An unexplored approach was presented in this work, focusing on coprocessing in atmospheric and vacuum distillations using Aspen Plus® V11 simulations. Between 5.86 and 15.41 wt.% of biogenic compounds was achieved in naphtha, kerosene and diesel fractions on average. Desalting unit was the major bottleneck to co-distillation with 51.57 to 58.22 wt.% feed renewable content lost in aqueous waste stream, followed by avg. additional energy specific input ranging from 0.26 to 5.26 GJ.tonne⁻¹. Highest renewable recovery and lowest additional energy input was observed for blends with intermediate density crude oils (20 - 25 °API).

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Keywords coprocessing, bio-oil, eucalyptus, simulation, distillation, RenovaBio

1. Introduction

Between 2011 and 2020, biofuels production around the globe increased from approximately 108 to 151 Mm³ (36%)¹. Brazil contributes to this increase with an increase of approximately 53.5% (25.6 to 39.2 Mm³) and presents clear growth trend for the sector in the next decade². In general, renewables have been used as standalone fuels or in blends with fossil correspondents (e.g., E100 and E27), strategy referred by the National Advanced Biofuels Consortium (NABC) (USA) as coprocessing by insertion point 3 or finished products blending. Differently, insertion points 1 and 2 corresponds to the blending of renewable fluids with non-finished products, in earlier stages of crude oil and intermediates fractions processing, respectively, which is commonly referred as coprocessing³.

Coprocessing with intermediates has been investigated focusing mainly in two different methods. The first is blending of hydrogenated vegetable oil (HVO) into fossil diesel range petroleum fractions, which is still under development and tests due quality standards concerns. The second route is the fast pyrolysis or hydrothermal liquefaction products blending with gas oils. Hydrothermal liquefaction (HTL) decomposes biomass to 250 – 300 °C and 100 – 150 bar in the presence of solvents such as water or ethanol. Apart from producing a considerably more stable fluid than the fast pyrolysis process, HTL is costly due to the severe conditions, therefore slowing down development of the topic, which still remains on pilot scale.⁴

Differently, fast pyrolysis process is less severe (1 to 5 bar, 350 to 500 °C, inert atmosphere)^{5,6} and more profitable (considering technological maturity)^{3,7}, already applied in commercial scales to produce bio-oil⁸, biochar and syngas⁶, the two last products usually destined to heat integration in circulating fluid-beds and CHP cycles^{9,10}.

Fast pyrolysis bio-oil (FPBO) is acidic, unstable, mixture of chemically diverse hydrocarbons generated from the thermochemical decomposition of biomass⁶. The depolymerization, dehydration and decarboxylation reactions generate highly oxygenated acids, aldehydes, phenols, sugars and oligomers, composing a multi-phase emulsion that destabilizes in exposure to air and mild temperatures¹¹. An upper layer is an organic, acidic phase, rich in lower molecular weight extractives. Middle layer is composed by an aqueous phase, with high solubility of sugars and light oxygenated compounds. Lastly, the bottom, viscous organic layer is rich in lignin derived components and phenolics.¹² This multiphase behavior varies subject to many compositional parameters, such as ash and water contents, as well as operational parameters such as the method of bio-oil condensation.¹¹

FPBO composition is highly dependent on feedstock used and pyrolysis process conditions.¹³ Wood-produced bio-oils present yield inversely dependent both to biomass particle size and catalytic reactions, this last parameter responsible for generating higher amounts of water in liquid product.^{5,14} Moreover, several studies reported higher contents of carboxylic acids, furans and ketones in forestry feedstock bio-oils (specially eucalyptus), while agriculture biomass tend to generate bio-oil with more phenolic groups.¹⁵ The chemical structure influence was also observed in bio-oil yield, being reported a higher bio-oil formation in hardwood (e.g., eucalyptus) than softwood (e.g., pine) most likely due to lower activation energy of wood structure in pyrolysis reactions.^{16,17}

In Brazil, with climate, land extension and technological advantages^{18,19,20}, there are several potential feedstocks for biofuels or intermediates production. Along with sugarcane and soybean, already extensively used for bioethanol and biodiesel production, respectively, softwood and hardwood are abundant for cellulose and wood production and potential candidates for bio-oil feedstock.^{21,22,23,24}

Identifying this potential, a promising route was explored by Petrobras, coprocessing pine wood FPBO with vacuum gasoils (VGO) in a Petrobras (Brazil) demonstration-scale FCC unit. The experiment exposed a clear possibility of renewable fractions produced for gasoline and diesel, with minor quality impacts up to 10% input renewable content. However, improvements are being developed, as the same group also traced renewable carbon throughout the experiment, acknowledging that only 30 to 40 wt.% was present in the finished liquid product.^{8,25,26}

Opposingly, insertion point 1 (distillation) has almost not been explored in literature, neither theoretically or experimentally, with only few studies showing low distillation temperatures and vaporized yields (e.g., < 40 wt.%), percentage slightly increased up to 67 wt.% with molecular distillation and up to 72 wt.% with hybrid, mathematical-empirical models for bio-oils in general.^{27,28,29,30} This percentage was also achieved with wood biomass (pine and cedar) bio-oils distillation experiments, limitation that correlates to polymerization of sugars and lignin oligomers, increasing boiling point and viscosity significantly.^{31,32,33}

Apart from distillation, FPBO is not miscible in crude oils, separating phases in lower °API crudes and creating emulsions in heavier crudes at low blending ratios, which is reported to potentially improve processability by lowering viscosity.^{34,35,36,37} Due to this challenge, surrogate-composition of bio-oil is often used in simulations, as a fairly precise method of representing fluid's properties.^{23,38,39,40,41,42,43,44,45,46,47} These simulations, however, are focused only on wood pyrolysis and further bio-oil upgrading, without distillation detailing. Also, no coprocessing simulations of crude oil and bio-oil are reported.^{42,48,49,50,51,52,53,54}

Therefore, the aim of this study was to close this simulation gap, coprocessing distillation of surrogate eucalyptus bio-oil components with selected Brazilian crude oils, including desalting, atmospheric distillation and vacuum distillation units. Besides mass and energy balances, this work also focused in distilled fractions' properties and renewable content recovered.

2. Materials and Methods

2.1. Surrogate eucalyptus fast pyrolysis bio-oil (FPBO)

Surrogate composition of eucalyptus bio-oil algorithm was defined investigating chromatographic analysis from several different studies.^{39,56,57,58,59,60,61,62,63}, as well as pyrolytic decomposition routes for heavy components screening.^{65,66,67,68,69}

Multi-objective optimization of molar ratios was performed ($1.35 < H/C < 1.50$ and $0.35 < O/C < 0.45$), using avg. chemical groups mass fractions from literature and varying constraints: chemical groups of water wt.% ($18 < \text{wt.\%} < 25$), sugars wt.% ($5 < \text{wt.\%} < 18$), lignin derived heavy components wt.% ($5 < \text{wt.\%} < 20$) and lignin derived heavy components wt.% in final mixture ($5 < \text{wt.\%} < 15\%$) constraints. All other chemical groups' wt.%, initially estimated as averages from literature sources, were proportionally adjusted so mixture's sum of groups wt.% achieved unity. All other components' wt.% not constrained derived from this adjustment and its selection and contribution calculation method is described below.

A total of 13 chemical groups were achieved for the final mixture: acids (7.67 wt.%), alcohols (1.06 wt.%), aldehydes (1.02 wt.%), aromatics/furans (2.60 wt.%), ethers (1.57 wt.%), esters (1.72 wt.%), nitrogenated (0.49 wt.%), hydrocarbons (1.58 wt.%), ketones (4.24 wt.%), phenolics (17.52 wt.%), sugars (18.00 wt.%), lignin derived heavy components (18.12 wt.%) and water (24.40 wt.%). The global average molar weight (MW) and boiling point (BP) among all sources, were calculated accounting each component reported, except for lignin derived heavy compounds.

To prevent the need to consider all components in each group, which would limit feasibility, 40 compounds were selected for optimization, based on common report between references used and constrained among components with mass fractions equal or above 1.00 wt.% in the bio-oil sample reported. The wt.% contribution of these selected components in each chemical group was defined by solving both linear and non-linear combination equations of pure components' MW and BP, respectively, matching global average MW and BP for each group.⁶ This method was not applied to lignin derived components, which were specifically selected solely through pyrolytic route of decomposition and literature analysis and given equal initial wt.% contribution.

The achieved wt% contribution of each component in its chemical group were: acids: acetic acid (73.98%), 4-hydroxy-3-methoxy-benzoic acid (8.55%), propanoic acid (17.47%); alcohols: 2-furanmethanol (24.87%), methanol (44.87%), 3-buten-2-ol (30.26%); aldehydes: furfural (8.40%), formaldehyde (10.72%), glutaraldehyde (80.87%); aromatics/furans: furan (17.69%), 2,3-dihydrobenzofuran (37.86%), 1,2,4-trimethoxybenzene (44.45%); ethers: eucalyptol (100%); esters: 1,2-dimethyl-propyl acetate (40.06%), octyl acetate (59.94%); nitrogenated: 2,4,6-trimethylpyridine (73.68%), dibenzopyrrole (26.32%); hydrocarbons: 4-ethenyl-1,4-dimethylcyclohexene (50%), 1-ethyl-1-methyl-cyclopentane (50%); ketones: 2-(3H)-dihydrofuranone (11.85%), 3-hydroxy-2-methyl-4H-4-pyranone (35.33%), 3-methyl-1,2-cyclopentanedi-one (46.57%), 1-hydroxy-2-propanone (6.25%); phenolics: 2-hydroxyphenol (30.37%), 2-methoxy-4-(prop-1-en-1-yl)phenol (16.59%) 4-hydroxyphenol (11.23%), 2,6-dimethoxyphenol (17.12%), phenol (24.70%); sugars: levoglucosan (21.02%), β -D-arabinopyranose (54.67%), cellobiose (24.31%); lignin der.: 2,6-dimethoxy-4-(3-hydroxyprop-1-enyl)phenol (12.5%), 2-methoxy-4-(3-hydroxy-1-propenyl)phenol (12.4%), 4-(3-hydroxy-1-propenyl)phenol (12.5%), 3,5-dimethoxystibene (12.52%), dehydroabietic acid (12.53%), dibenzofuran (12.53%), pinosresinol (12.51%), 2-phenyl-2,3-dihydro-1-benzofuran (12.52%). Component wt.% in final mixture was finally achieved multiplying each component contribution in its group by the chemical group wt.% in the mixture.

The final mixture, was inserted in Aspen Plus® V11 for equilibrium and properties calculations through UNIFAC model and NIST empirical correlations present in the software. Each component's chemical structure and its correspondent UNIFAC contribution groups were inserted manually when missing, parameters requested for properties estimation through Aspen's Property Constant Estimation System (PCES). Pinosresinol and 2-phenyl-2,3-dihydro-1-benzofuran were inserted as pseudocomponents, with chemical structure, MW and BP as required inputs retrieved from literature.⁶¹ Other than these, an extensive listing of all UNIFAC parameters or group contributions would not be possible given the size of this work, and it is left

for the reader's calculation, since the VLE model is widely known, the selected components were provided and its structures are easily found in open-access databases.

2.2. Brazilian crude oils

Three different crudes were investigated in three conditions (0, 5 and 10% renewable blend, i.e.: 0, 20 and 40 kbbbl.day⁻¹). These scenarios used specifically selected light, medium and heavy crude oils as main blends' constituents: Iracema field (2016) (32.6 °API), Lapa field (2011) (22.8 °API) and Peregrino field (2016) (13.2 °API), respectively. The blends were labeled with "L", "M" or "H", plus the percentage of the crude present, plus "R" followed by the percentage of renewable content (e.g., L095R005; Light crude 95vol%, Bio-oil 5vol%).

Lapa field data was retrieved from Total Energies Assay Database (publicly available), the company is the field operator (45%), together with Shell Brasil Petróleo (30%) and Repsol Sinopec Brasil (25%). Iracema field data was retrieved from Aspen Hysys® Assay Database and is operated by Petrobras (65%), Shell Brasil Petróleo (25%) and Galp Energia (10%). Peregrino field data was retrieved from Equinor Assay Database (publicly available), the current operator (60%) along with Sinochem (40%).

2.3. Aspen Plus® V11 process design

Process was designed to represent a large 63594.92 m³.day⁻¹ (400 kbbbl.day⁻¹) refining unit (the largest in Brazil) with a wide range of products. All operational parameters are detailed in Fig 1 and all columns and heat exchangers were modelled as Aspen's PETROFRAC and HEATER units, respectively. Cut temperatures of T5vol.% and T95vol.% were defined, in °C, as: untreated LPG (IBP – 32), Light Unstabilized Naphtha (LUN) (32 – 193), Heavy Unstabilized Naphtha (HUN) (85 – 193), Kerosene (KER) (193 – 271), Diesel (DSL) (271 – 350), Atmospheric Gasoil (AGO) (350 – 425), Light Vacuum Gasoil (LVGO) (425 – 510), Heavy Vacuum Gasoil (HVGO) (510 – 565) and Vacuum Residue (VCR) (565 – FBP).

Several sources were used for simulation settings.^{69,70,71} Top and side distillates flowrates were varied to achieve maximum product flowrates, subject to each product T95 vol.% +/- 5 °C for light and medium blends and T95 vol.% +/- 15 °C for heavy blends. In this work, no heat integrations were designed, although total energy performances were evaluated.

Desalting unit was designed as a vapor-liquid-liquid equilibrium separation stage (FLASH3 in Aspen), focused on water and water-soluble components removal. Wash water was fed to the system, which liquid flow was minimized by monitoring input blend water content to achieve 5 vol% water in total mixture. Pre-Flash Unit (PFU) was modelled with 10 stages to improve refinery yields and economics^{72,73,74}, recovering Untreated LPG and Unstabilized Naphtha (LUN). The naphtha stabilization process was not designed in this work. Crude Distillation Unit (CDU) was designed with 35 stages, three side strippers and three pumparounds, recovering Heavy Unstabilized Naphtha (HUN), Kerosene (KER), Diesel (DSL) and Atmospheric Gasoil (AGO) fractions. Wet Vacuum Distillation Unit (VDU) was designed with 9 stages, top partial vapor condenser (vacuum system), two pumpbacks and two pumparounds, producing Light Vacuum Gasoil (LVGO), Heavy Vacuum Gasoil (HVGO) and Vacuum Residue (VR) fractions.

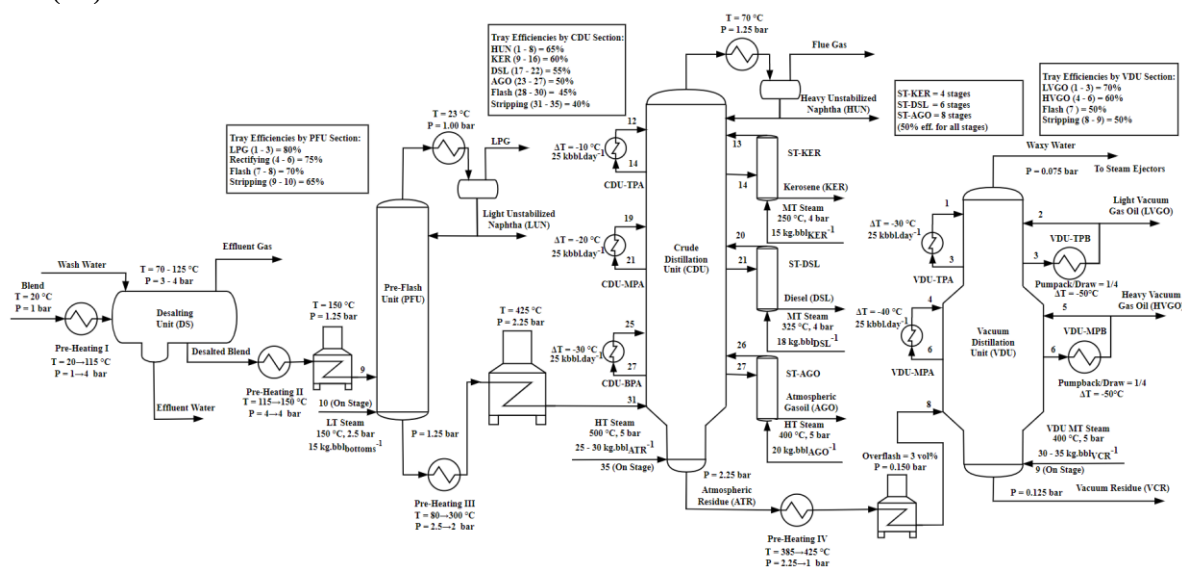


Fig. 1 Process Flow Diagram of Aspen Plus® Simulation Scenarios

3. Results and discussion

3.1. Surrogate eucalyptus fast pyrolysis bio-oil (FPBO) and Brazilian crude oils

FPBO modelled was analyzed in Aspen Plus® V11 generating the true boiling point (TBP) distillation curve present in Fig. 2. In the same plot, extended Mante et al.³¹ and Varma et al.³² data are compared with EUC24 (24 wt.% water) bio-oil modelled.

Literature data existent on bio-oil, however, only presents catalytic fast pyrolysis of pine (temperatures 425 °C and 465 °C)³¹ and conventional fast pyrolysis of cedar³², both softwoods that differs from eucalyptus hardwood. EUC24 presented higher distillation similarities with cedar wood bio-oil, in non-catalytic pyrolysis conditions³². The highest differences can be observed in T10-30vol.% range, affected primarily by water content, and in T95-T100vol.% range, directly correlated to the heavy model compounds used, which also impacted reported viscosity. EUC24 presented H/C = 1.403 and O/C = 0.433, while Mante et al.³¹ reported H/C = 1.193/1.233 and O/C = 0.357/0.239 (38.89 % and 94.96 % difference from EUC24), and Varma et al.³² H/C = 1.469 and O/C = 0.437 (5.41 % average difference from EUC24). Molar ratios, along with water and nitrogen contents, also indicates more similarity to cedar oil in terms of composition, which can be explained by the fact that catalytic bio-oil has improved quality presenting lower O/C and N/C ratios, focusing on hydrotreatment processes, however, it decreased energetic potential by also partially reducing H/C ratio.⁷⁵

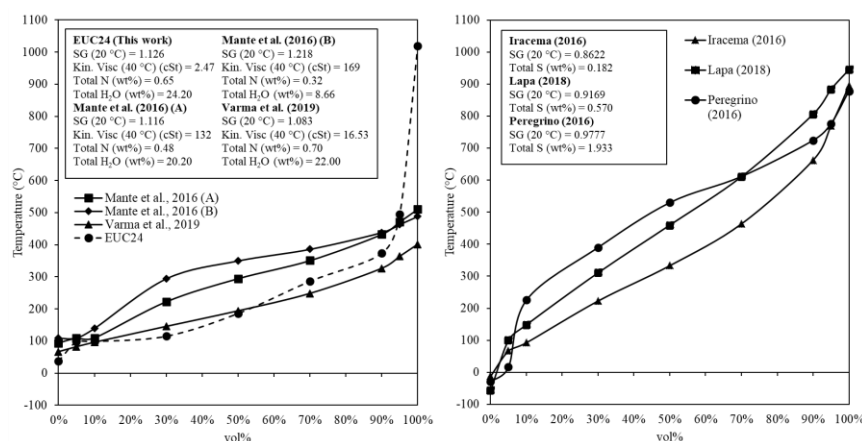


Fig. 2 TBP distillation curves comparison of eucalyptus bio-oil EUC24 (this work), literature pinewood catalytic³¹ and cedarwood bio-oil³² (left) and selected crude oils TBP distillation curves (right).

3.2. Co-processing Analysis

As expected, phase separation occurred, dividing part of the renewable feed. A 3-phase system (negligible gas phase) was formed in the desalting unit, with highest biogenic carbon losses in heavier blends feeds (53.2 wt.% and 58.2 wt.%, 5 wt.% and 10 wt.% blends, respectively). Medium blends presented the lowest losses, (51.6 wt.% and 56.3 wt.%) which could be explained by molecular similarities to EUC24's (8 carbons in avg.), preventing phase migration.

This hypothesis for medium blend was supported by the relative renewable recovery (Table 1), pointed as 9.25 wt.% avg. for LUN, HUN, KER, DSL fractions (C5 – C25), especially in HUN (10.72 wt.%). Although present in all types of blends, this compatibility is potentially more recurrent with intermediate crudes, with higher renewable content present scattered along different fractions. This effect was not linear and variable between types of crudes since, apart from presenting higher overall recovery for medium blends, fractions biogenic percentage was counterbalanced by higher flows (LUN, HUN, KER and DSL avg. 9.67 wt.% vs 15.41 wt.% compared to heavier blends) (Fig. 3). Therefore, there is an optimal point of conciliation between elevating a fraction output and its renewables percentage, combining different types of crudes, which is of summary importance towards carbon credits pricing.

Table 1. Renewable content as wt.% from total recovered, achieved in each scenario (excluded total fossil scenarios)

Scenario	LPG	LUN	HUN	KER	DSL	AGO	LVGO	HVGO	VCR	Ren. Output (tonne.day ⁻¹)	Ren. Input (tonne.day ⁻¹)	Recovery (%)
L095R005	28.98	5.08	5.51	5.22	1.04	2.29	0.24	0.52	0.44	1293.90	2727.26	47.44
L090R010	37.33	9.51	9.02	9.36	2.14	5.21	0.22	1.07	0.93	2335.92	5454.52	42.83
M095R005	16.05	10.83	8.50	6.71	1.43	1.88	0.05	0.42	0.24	1316.48	2727.26	48.27
M090R010	27.63	16.32	10.31	16.25	4.02	3.81	0.08	0.79	0.50	2371.04	5454.52	43.47
H095R005	4.66	16.44	22.58	7.74	1.05	2.58	0.08	0.15	0.23	1230.43	2727.26	45.12
H090R010	8.75	22.05	31.04	19.56	2.80	4.90	0.23	0.33	0.48	2201.67	5454.52	40.36

Another important result observed was that for heavier blends, elevated losses to flaring are verified. This due to poor top product separation mainly on PFU and CDU, stripping lighter components of bio-oil rather than incorporating it to naphtha fractions, equilibrium effect potentialized by lower flows of these products on heavier blend cases. Since modelled bio-oil has approximately 9.15 wt.% of < C4 hydrocarbons, part of this mass would inevitably be lost to flaring rather than incorporated to LPG fraction, even for lighter blends. Several CCS (Carbon Capture and Storage) strategies are being investigated worldwide to mitigate flaring due to environmental concerns, therefore blending solely with heavier crudes would be, preliminary, not advised.

Regarding energy efficiency, lighter combinations, presented significantly lower additional energy input per tonne produced, a difference ranging from 1.53 to 3.18 GJ.tonne⁻¹ between lighter and heavier blends for 5 and 10 vol.% ratios, respectively. The main reason behind this observation was the higher efficiency of the pre-flash unit, increasing product recovery as well as removing part of the water entrained in the blend, which was not observed in heavier blends. In those cases, PFU performance was poor due to low light components in the mixture to be stripped. The remaining water led to higher energy consumption in the heat train leading to CDU and its furnace, although water levels for all product fractions (excluding LPG) were still below 1 wt.%. Optimal removal was spotted for medium blends between 0 and 5 vol.%, reinforcing the hypothesis of improved compatibility facilitating separation. As this compatibility effect and the water mass balance were observed as of high importance, further studies are needed to clearly understand its impacts, in the same way as the ones of a complete heat integration between the units.

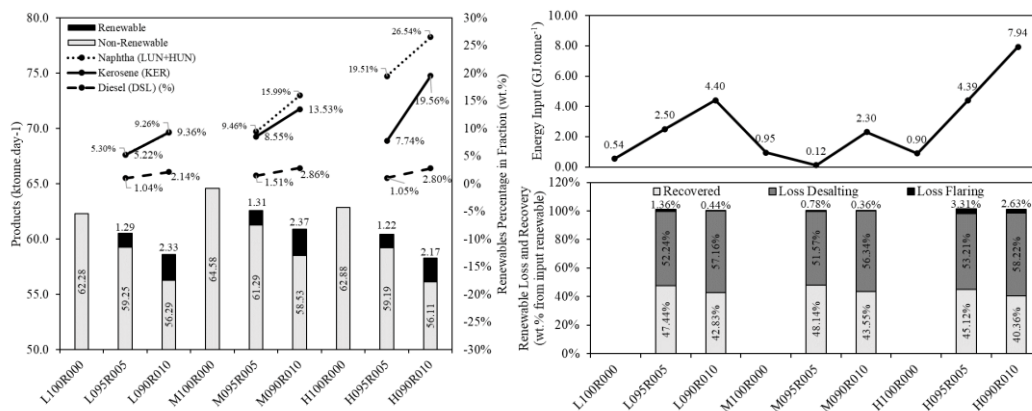


Fig. 3 Renewable/non-renewable production and renewable content in products of interest (left) and energy input relative to production (top right) and renewable recovery/loss profiles (bottom right).

4. Conclusions

Coprocessing is one of the most promising routes for renewable fuels and chemicals in the near future in Brazil. Policies and fundings are focusing on enabling advanced coprocessing biofuels for carbon credits eligibility. Simulations, like the one presented, could support operations by acting as soft sensors for renewables inferential accounting. This study has shown part of this development, with concrete modelling of eucalyptus bio-oil, matching properties from experimental data. Further development is needed towards viscosity values, which depends highly on heavy unknown components. Also, Aspen Plus® coprocessing simulations indicated that pre-salt's medium °API crude could be the best blend option, providing on average 9.67 wt.% biogenic carbon presence among LUN, HUN, KER and DSL fractions. However, improvements are still needed, as more than 50 wt.% of renewable content is lost in desalting and flaring, and heat integrations impacts are still not fully understood.

Acknowledgements

The authors thank the São Paulo Research Foundation (FAPESP) – grant #2015/20630-4 and School of Chemical Engineering, University of Campinas, by the infrastructure and AspenTech by the Aspen Plus® software academic licenses supplied.

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